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Synthesis and characterization of copper nanoparticles/polyvinyl chloride (Cu NPs/PVC) nanocomposites

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Abstract

In the present work, two-synthesis method for copper nanoparticles (Cu NPs) in polyvinyl chloride polymer (PVC) has been developed by adding previously synthesized NPs to the resin and by an in situ synthesis of the NPs. The resin was mixed with additives to enhance obtaining a pasty mixture called plastisol. The obtained plastisol is liquid at room temperature and have viscoelastic and pseudoplastic properties. The plastisol showed changes in its mechanical properties by heat action, like a remarkable increase of viscosity at high temperatures, passing from the initial liquid state to solid state at curing temperature (180–200 °C). Cu NPs were synthesized previously by microwave assisted polyol method, using copper acetate (CuAc₂) as precursor, ascorbic acid (AA) as reducing agent, polyvinylpyrrolidone (PVP) as stabilizer and ethylene glycol as solvent. In this synthesis ethylene glycol (EG), a diol widely used in polyol method; was used as a solvent. Microwaves provided thermal heating, an alternative to the conventional heating by convection. The microwave irradiation was successfully used to warm dielectric materials, considering the property of tangent loss ($\tan \delta$), the higher the value, the greater transformation of electromagnetic microwave energy into heat energy was achieved, this one occurs preferably in polyol, such as ethylene, which has high dielectric constant. Different concentrations of plasticizer and several temperatures were evaluated for curing nanocomposites (Cu NPs/PVC). To obtain films of Cu NPs/PVC, a coating technique over a substrate (paper or fabric transfer) was used. Films were prepared in order to produce a material with further bactericidal activity. The characterization was performed by X-Ray diffraction and ultraviolet visible spectrophotometry.

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1. Introduction

Thermoplastics functionalized with copper nanoparticles are of great interest because of its many applications such as medical items, cleaning, antiseptics, textiles, paintings, intrahospital coatings, coatings handrails on public transportation, etc. The antibacterial effect of copper nanoparticles has been reported by Yoon et al. (2007) and Cioffi et al. (2005). In preparation of nanoparticles the size requirement is not enough, it is necessary a procedure that assures a tight distribution of size particle, a controlled morphology and composition and identical crystal structure. Chemical methods provide better control to achieve these characteristics. One of them is the polyol method [Brayner et al. (2013), Shankar and Rhim (2014), Gurav et al. (2014), Fievet et al. (1993), Park et al. (2007a) and Park et al. (2007b)]. This method is characterized by using alcohols as solvents, generally diols as ethylene glycol, propanediol or diethylene glycol. They can dissolve several inorganic precursors, in addition, they act as reducing and chelating agents. Therefore, a fast nucleation and slow growth of particle is accomplished at specific temperature. By this method, it has been possible to obtain metal nanoparticles and metal oxides with low distribution of size and controlled morphology. This method is already known to obtain metal nanoparticles and metal oxides with low distribution of size and controlled morphology, although in recent years some variants have been reported as the polyol method via microwave [Zhao et al. (2004), Kawasaki et al. (2011), Nishioka et al. (2013), Nikkam et al. (2014), Valodkar et al. (2014) and Hong et al. (2002)].

Recently it has been reported the synthesis of several nanocomposites, such as Cu NPs/PVC [Becerra et al. (2013)], copper nanoparticles in high density polyethylene Cu NPs/HDPE [Molefi et al. (2010)] and copper nanoparticles in polypropylene (Cu NPs/PP) [Pinochet (2012)] synthesized by molten state method and incorporating the copper nanoparticles. It has also been reported on the “in situ” synthesis copper nanoparticles in polystyrene (Cu NPs/PS) from the polymerization of styrene monomers [Konghu et al. (2012)]. Unlike the above polymers PVC is a thermoplastic (it is softened by heating and can be easily molded and retain the new shape recovering its initial consistency when it is cooled), so is possible to obtain in rigid or flexible forms depending on their formulation and transformation. This is the reason because that the polyvinyl chloride is one of the most important synthetic materials at world market after polyethylene.

The aim of this study is to evaluate the synthesis “ex-situ” and “in-situ” of nanocomposites Cu NPs/PVC for a potential development of films with antibacterial properties.

2. Experimental

2.1 Materials

These reagents were not modified; resin (PVC G-68, Mexichem); dioctyl phthalate plasticizer (DOP, ESBO Chemical Company); liquid stabilizer (LX-410 Chemical Company); anhydrous copper acetate (CuAc_2 , technical grade); ascorbic acid (AA, $\text{C}_6\text{H}_8\text{O}_6$, Sigma Aldrich); polyvinylpyrrolidone (PVP = 45,000 g/mol, Sigma Aldrich) and ethylene glycol (EG, Merck Millipore).

2.2. Preparation of plastisol PVC

The composition mixture is generally expressed in units "per hundred resin" (phr), where a certain amount of additive is indicated per 100 parts of resin (UNE 53-46290). The plastisol is obtained by mixing the PVC resin with 80 phr of DOP and 2.5 phr of the stabilizer in a glass reactor of 500 ml capacity. With the immersion mixer incorporated in the reactor, the plastisol was stirred at 400 rpm for 10 minutes or until obtaining a homogeneous paste. After the mixing step, the procedure continuous to remove air bubbles from PVC mass. Vacuum is applied through a connector to eliminate the air trapped into the paste mass-produced by the movement of the blades of the mixer, and the swelling reaction of PVC resin by plasticizer addition. The equipment used was a Schlenk line connected to a vacuum pump Vacuubrand RZ 2.5 with a maximum vacuum of 2×10^{-3} mbar.

2.3 Synthesis of Cu NPs by polyol method via microwave

AA was dissolved in 5 mL of EG, then was added PVP and 10 mL of EG again; the solution formed was stirred no more 500 rpm by 15 minutes approximately, and heated at a constant reflux. It was accomplished by using microwave equipment adapted for chemical synthesis; microwave heating is carried out for 20 min. In this stage a solution of CuAc_2 in ethylene glycol was added through a Schlenk funnel three or six minutes after starting the microwave heating.

By performing this method the reducing agent is in excess in the initial solution as long the precursor solution is added to it, therefore the reaction of reduction of the Cu^{+2} ions is made directly. Cu NPs in solution are centrifuged at 10,000 rpm in a high-speed centrifuge, rinsed with acetone, and centrifuged again and a reddish powder is obtained.

2.4. Ex-situ synthesis of Cu NPs/PVC nanocomposites

Cu NPs powder obtained was used to prepare nanocomposites of Cu NPs/PVC by the sol-gel method. In this method, firstly a solution or PVC plastisol solution is formed, then Cu NPs 1% weight of plastisol is dispersed using a magnetic stirrer for 30 minutes or until uniform distribution of the solution. This solution was poured on a transfer paper using an application die of defined thickness (15 in.). Curing or gelling of the plastisol is performed in a stove at a temperature of 180 °C with a residence time of 3 minutes. The laminates of the nanocomposites of Cu NPs/PVC come off the paper and they are let cool.

2.5. In-situ synthesis of Cu NPs/PVC nanocomposites

In situ impregnation of copper nanoparticles in the PVC polymer matrix is performed by the sol-gel method. In a four-necked ball; 3.4 g of PVP and 10 g of DOP are added, the mixing is made using an ultrasonic tip for 15 minutes. Then a solution containing 0.47 g of CuAc_2 in 10 g of DOP and is mixed for 1 hour. Next, a solution containing 0.92 g of AA in 10 g of DOP is added and mixed for 30 minutes. The molar ratios were $[\text{CuAc}_2/\text{PVP}] = 7.6$ and $[\text{AA}/\text{CuAc}_2] = 2$. Finally, PVC resin with 2.5 phr of stabilizer is added and the reaction time of 2 hours is completed. The procedure for air extraction from plastisol is performed. The curing thus obtained is performed at the same previous conditions.

2.6. Characterization

The UV-Vis spectra were obtained with a spectrophotometer UV-Vis model Genesys S10 (Thermo) single beam using a light source xenon lamp flash UV-Vis with a range from 190-1100 nm. Crystallinity and phase composition of the copper nanoparticles were investigated by X-ray diffraction (XRD) using a X-rD8-Focus (Bruker) diffractometer operated at 40 kV, 40 mA with θ -2 θ geometry and Cu radiation (K-alpha 1, $\lambda = 0.154018$ nm), "slit" receptor 0.1 mm, "slit" 1 mm divergence and "soller" 2.5°, scintillation detector. The XRD patterns were recorded in the 2 θ range of 10° to 60° in steps of 0.04°.

3. Results and discussion

3.1. Time influence microwave radiation on synthesis of Cu NPs

Because the reducing agent is initially under microwave irradiation and having a higher power cycle, the solution absorbs more radiation and the reducing agent reacts with the environment decreasing its reducing power, so the reduction reaction towards nanoparticles formation is not favorable. In this case, the time of preferable addition is three minutes, in a higher addition time; there is a longer exposure of microwave radiation for the reducing agent producing the same effect already mentioned.

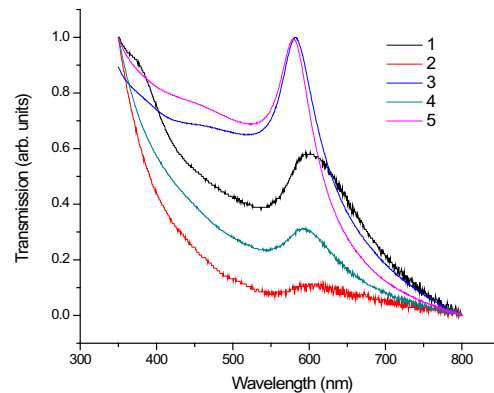


Fig. 1. UV-Vis spectrum of Cu NPs for procedure polyol method via microwave.

3.2. Influence of the reducing agent in the synthesis of Cu NPs

Fig. 1 shows that the plasmon of Cu NPs is more acute in 5 and 3 samples followed by the sample 1, this indicates indirectly that these nanoparticles have a minor size of particle that in other samples, so the optimal molar ratio of reducing agent to the precursor is 5, when the molar ratio is 8 this effect does not improve, while when the molar ratio is 2.5, this effect decreases, this result is agree with the results of the antecedents, since in the method of synthesis of nanoparticles of copper by polyol the conventional heating is used, the optimal molar relation AA to reducing agent is of 8, and when the heating is through microwaves this value decreases.

Table 1. Experimental tests of Cu NPs preparation.

	1	2	3	4	5
AA [mM]	0.013	0.028	0.028	0.016	0.045
PVP [mM]	2.216	1.16	0.502	3.79	1.102
CuAc ₂ [mM]	1.98	6.061	5.51	4.4	5.73
t(min) adds CuAc ₂	3	6	3	6	3
χ AA/CuAc ₂	2.5	2.5	5	5	8
%P Cycle Microwave	50	50	20	50	20
Absorption peak (plasmon)	Yes	No	Yes	Yes	Yes
λ max of peak (nm)	595.5	439.5	581.5	590.5	579

3.3. Characterization of Cu NPs by XRD

The XRD pattern is shown in Fig. 2 and compared with the standard pattern number 4-836, confirming the cubic face centered (fcc) structure of Cu⁰. The two intense peaks of the spectrum match with two of its three signals of the characteristic pattern of diffraction for the Cu⁰, at $2\theta = 43.37^\circ$, 50.53° and 74.12° , corresponding to (111), (200) and (220) crystal planes, respectively. This confirms the formation of nanoparticles of pure copper with cubic face-centered structure (fcc cubic system, Fm-3m space group No. 225, $a = 3.6150 \text{ \AA}$, $D = 8.950 \text{ \AA}$).

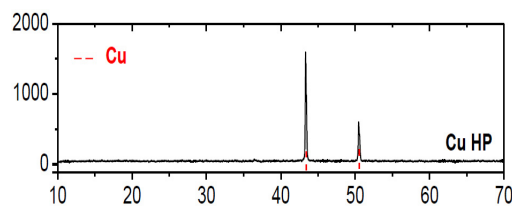


Fig. 2. XRD of Cu NPs to procedure by polyol method via microwave.



Fig. 3. (a) CuAc₂/PVC and (b) Cu NPs/PVC.

3.4. Cu NPs/PVC XRD characterization

Fig. 4(a) shows a common plastisol, which became a gel at 180 °C with a residence time of 3 minutes. During processing of flexible PVC, by any route, initial mixing of PVC particles in the liquid plasticizer, passes through two processes gelation and fusion. During the gelation process, the plasticizer is absorbed by the PVC particles and diffuses through them, swelling them. Inside reactor occurs a complex process where the shear rate developed by the mixer affects the rheological behavior of plastisol. Shear rate developed by mixer and the order in which the ingredients are added can in addition affect to the rheological behavior of plastisol. The interactions that take place between the plasticizer and the resin yield the gel behavior and fusion, reason why the knowledge of the nature of these interactions is fundamental. Fusion is the process where as a result of heating (typically around 160 °C), the PVC particles and the plasticizer are fused and mixed thoroughly to form a homogeneous material. This material is able to develop its mechanical properties completely. The Fig. 4(b) corresponds to plastisol with 1% of CuAc₂ and is observed the turquoise green color characteristic of the copper salt. Fig. 4(c) corresponds to plastisol prepared following the propose methodology in this research. When finalizing the preparation of plastisol additive with CuAc₂, the PVP and the AA, this presents a green color that is changing to yellow and turns in red after adding the PVC resin. After 12 hours of rest of plastisol, very fine precipitate reddish is observed very fine, which us could indicate the metallic copper presence, as it is observed in the Fig. 4(d). The time of rest after adding the PVC resin is necessary, since when adding the resin this is swollen absorbing the DOP, so the speed of reduction of the copper ions increases.

For the formation of Cu NPs the AA plays an important role as reducing agent of the salt of copper, and in excess, is essential to avoid the oxidation of copper nanoparticles [Kawasaki et al. (2011)]. The antioxidating property of the AA comes from its capacity to capture free radicals by means of the electron donation, as it is outlined in Fig. 5.

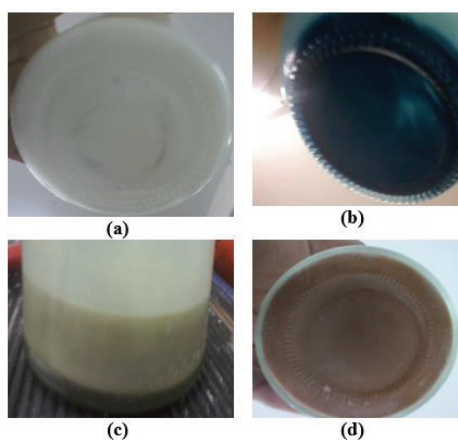
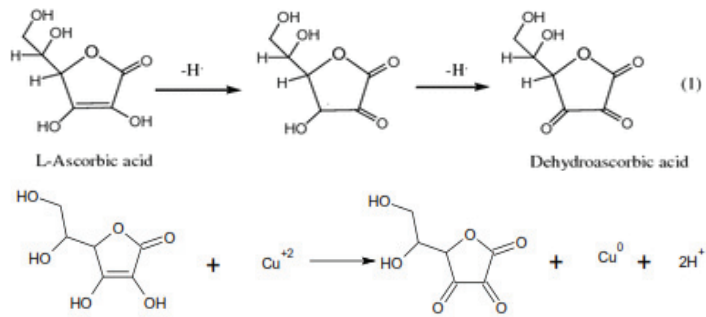


Fig. 4. (a) M1; (b) M2; (c) M3; (d) M4.

Fig. 5. Scheme of AA reactions with Cu^{+2} .

The PVP is used as an antibinder or dispersing agent that stabilizes copper nanoparticles, and the size and the form of nanoparticles are going to depend strongly on the concentration of the antibinder. The PVP has the structure of a polyvinyl skeleton with polar groups of oxygen and nitrogen, that have pairs of free electrons to donate and form an interaction coordinated with copper ions, creating therefore the compound of PVP-Cu^{+2} , as it is outlined in Fig. 6, reaction 2. This fact indicates that the complex of PVP-Cu^{+2} is reduced to PVP-Cu^{+1} in the first place, and then Cu^{+1} , reason why the celestial colour of the reaction system happens to yellow colour and after to red after a greater reduction of Cu^{+1} to Cu^0 as it is observed in the Fig. 4(d), nevertheless with the help of the temperature in the cured process of, not only the reddish colour is observed but that also is appraised the metallic brightness characteristic of copper.

Fig. 7 shows the XRD patterns of the PVC (M1) and Cu NPs/PVC (M4) films. A centered wide peak at 12.92° is identified, that corresponds to the amorphous matrix of PVC, and the percentage of crystallinity of the PVC is at the most the 12%. Also two peaks at 2θ are identified = 43.13° and 50.28° that corresponds to the reflections of Bragg of (111) and (200) of Cu^0 of centered cubic faces.

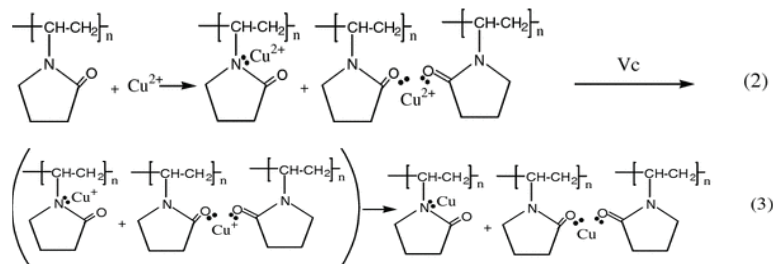
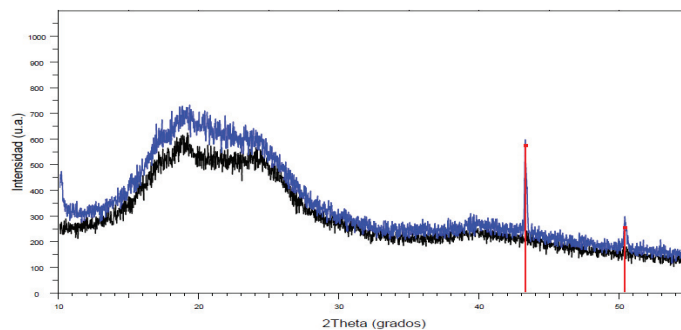
Fig. 6. Outlining PVP reactions with Cu^{+2} .

Fig. 7. XRD pattern of Cu NPs / PVC through the in-situ synthesis.

4. Conclusion

In the development of the ex-situ synthesis of compounds of Cu NPs/PVC it is indispensable to control the size and dispersion of Cu NPs, which occurs preferably when the precursor is added at three minutes. The optimal potential for the synthesis via microwaves is of 20% of cycle. The optimal molar relation between reducing and precursor agent is 5.

For the synthesis in-situ of compounds of Cu NPs/PVC the reduction of Cu^{+2} to Cu^0 it has been obtained with the addition of the AA which is corroborated with the XRD. This method has technological advantages on the other method because the present process of transformation of the PVC stays, which would facilitate a possible transference of technology. Nevertheless, it is pending a morphological study of the Cu NPs formed.

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